

**HYCSOS: A CHEMICAL HEAT PUMP AND
ENERGY CONVERSION SYSTEM BASED ON
METAL HYDRIDES**

by

**D. M. Gruen, I. Sheft,
G. Lamich, and M. Mendelsohn**

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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in collaboration with

L. Carlson,* A. Knox,* R. McBeth,
J. Nixon, and F. Schreiner

Chemistry Division

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*Engineering Division

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Dieter M. Gruen, Irving Sheft,
George J. Lamich and Marshall Mendelsohn

in collaboration with

Larry Carlson, Alvin Knox, Robert McBeth,
Jack Nixon and Felix Schreiner

ABSTRACT

The HYCSOS chemical heat pump and energy conversion system based on metal hydrides is described. The HYCSOS thermal energy storage and recovery modes; the chemical heat pump heating and cooling modes as well as the energy conversion mode are discussed in detail with the aid of heat transfer fluid and hydrogen flow diagrams. The thermodynamic efficiencies of the two metal hydride system are calculated for the heat pump and conversion modes.

Design and construction features of a demonstration test facility which utilizes four stainless steel tanks holding 10 lbs. each of either LaNi_5 or CaNi_5 are given. The operation, instrumentation and control of the system is detailed with the aid of photographs, drawings and a system layout diagram.

Initial operation of the system has shown that 33 moles of hydrogen can be transferred from CaNi_5 at $\sim 100^\circ\text{C}$ to LaNi_5 at $\sim 40^\circ\text{C}$ and recovered from LaNi_5 at $\sim 8^\circ\text{C}$ to reform CaNi_5H_4 at 40°C with cycle times approaching 2 minutes for 50% hydrogen transfer. The relevant data pertaining to these experiments are given in graphs and tables. The next phase of operations will be done on the fully insulated system to establish a firmer data base, obtain power balances and determine optimum operating parameters. In order to achieve these goals in a reasonable time frame, a data display and handling system is required.

A materials development program is being carried out concurrently with HYCSOS operations. Significant progress is being made in the development of

new, more cost effective alloy system displaying superior properties for heat pump action.

I. INTRODUCTION

About 25% of the total energy consumed in the United States is used for space heating and cooling for which highly concentrated (high temperature) sources are not required. Since second law energy utilization efficiency of the higher temperature fossil and nuclear energy sources for these applications is low ($< 10\%$), the use of lower grade heat sources would yield greater thermodynamic efficiency and conserve the dwindling supply of fossil fuels for applications where their replacement is more difficult.

Two major sources of energy are in principle very well adapted to these applications: reject heat from central power station operations and solar energy. The Argonne HYCSOS system, a two hydride concept for the storage and recovery of thermal energy for heating, cooling and energy conversion in an integrated system, is operational and preliminary results are described with the help of heat transfer fluid and hydrogen gas flow diagrams. Initial descriptions of the overall concept,¹ and a thermodynamic analysis of the efficiency of the energy conversion cycle have appeared² and the overall systems concept has been described.³ Certain special features associated with the use of metal alloy hydrides which make them virtually unique for solar energy applications may be pointed out.

Two aspects of solar energy, its diffuse and intermittent nature, dictate optimization of all of the systems employed in the utilization of this renewable resource. Although solar energy is usually considered to be ideally matched to the task of direct space heating, collector temperatures, particularly in the case of high performance collectors for space cooling purposes, exceed the requirements for optimum second law efficiencies. A system operating on the heat pump principle could make optimum use of higher collector temperatures to store thermal energy, for space conditioning and for reasonably efficient conversion of heat into work. The two metal hydride or HYCSOS concept is such a system and offers the possibility of reducing the required solar collector area by 40% compared to thermal storage systems not utilizing the heat pump principle. Because of the three possible modes of operation, HYCSOS can make flexible use of the widely varying supply of

solar energy. Furthermore, the use of heat transfer fluids allow ready substitution of alternate power for solar energy and efficient use of both energy sources for heating or cooling purposes because of heat pump operation. A hydride system for space heating and cooling involving the use of solar as well as alternate energy has often been considered and appears to be very attractive for use with the HYCSOS concept. (The hybrid nature of HYCSOS is indicated in the figures by inclusion of an alternate heater in the heat source loop). A hybrid system has the desirable feature of reducing the troublesome problems associated with long term or seasonal thermal energy storage.

Some of the special features associated with the HYCSOS concept for solar energy applications are listed below.

1. High second law efficiencies by heat pump action in both thermal storage and cooling modes can be achieved.
2. The consequence of heat pump action in the thermal storage mode is that collector temperatures ($\sim 140^{\circ}\text{C}$) can be used to decompose the high temperature hydride while at the same time using the heat of formation of the low temperature hydride at $\sim 50^{\circ}\text{C}$ for space heating. The full heat of formation of the high temperature hydride is recovered by heat pump action in the absence of insolation. If the solar collector is to provide one Btu for space heating during the day while at the same time placing one Btu into thermal storage, the theoretical reduction factor in solar collector areas is $1 - \Delta H_{\text{low}}/2\Delta H_{\text{high}}$. Since the ratio of the heats of formation of CaNiH_4 and LaNi_5H_6 are near unity, the solar collector area could be cut in half compared to collectors operating with non-heat pump storage materials.
3. In the cooling mode, direct conversion of thermal energy into cooling power by heat pump action can be achieved, thus circumventing, for example, conversion of solar thermal energy to work in a Rankine cycle for subsequent operation of the compressor of a conventional air conditioner.
4. Materials engineering can be applied to alloy hydride systems so as to "tailor" them for optimum performance over preselected

temperature limits. Operation between $\sim 100^{\circ}\text{C}$ and -20°C may become possible, offering the opportunity for space conditioning and refrigeration applications at modest collector temperatures.

5. Hybrid operation using both solar and an alternate energy source with high second law efficiencies provides the opportunity for minimizing long term thermal storage capacity while maximizing energy utilization in a flexible manner.
6. Operation in the energy conversion mode, if competitive with photovoltaic or other solar energy conversion schemes, could help to meet residential electrical energy needs. Much development work needs to be done in this applications area. The possibility of HYCSOS operation in heating, cooling and conversion modes in a single system provides an incentive to develop hydride technology for use in this flexible manner.
7. Since metal hydrides decompose over a range of temperatures, thermal storage is not critically dependent on collection temperature. These materials offer thermal storage capabilities achieved only in so-called "cascade" collection systems which employ more conventional thermal energy storage materials.
8. In common with other chemical bond storage materials, metal hydride storage materials require no insulation and provide indefinite storage of thermal energy.
9. The metal hydrides possess quite high volumetric thermal energy storage capacities and compare favorably with the best phase change media so far available.
10. The incorporation of heating, cooling and power conversion functions into a single system based on metal hydride technology may offer economic advantages over separate systems each designed to perform only one of these three functions.

II. PHYSICO-CHEMICAL PROPERTIES OF METAL-HYDRIDES SUITABLE FOR SOLAR ENERGY APPLICATIONS

Metal hydrides and, in particular, certain metal alloy hydrides are unusual among chemical compounds in undergoing reversible thermal decomposition with good kinetics. By varying the alloy composition, it appears now to be

possible to obtain materials possessing the pressure-temperature relationships desirable for purposes of solar energy applications. The two metal hydride systems to be described in this paper will be seen to offer several special advantages.

In recent years, lanthanide-nickel hydride systems have been investigated which have properties that make them attractive candidates for solar energy utilization purposes.

Van Vucht, Kuijpers and Bruning⁴ reported the ability of intermetallics of the form AB_5 , where A can be a lanthanide and B is nickel or cobalt, easily to absorb and reversibly desorb large amounts of hydrogen with excellent kinetics. These compounds have hexagonal structure. For example, stoichiometric $LaNi_5$ can absorb over six hydrogen atoms while undergoing a 25% lattice expansion. A two-phase region is bounded by solid solution at low H/M ratios and the hexagonal $LaNiH_6$ hydride phase at higher H/M ratios. The H/M range of the two-phase plateau region is shortened somewhat with increasing temperature. A hysteresis effect between the absorption and desorption plateau pressures increases with temperature and is probably related to the internal stresses associated with the large volume change on hydriding. Although temperature dependent, the kinetics of the system are rapid, with over 95% of the equilibrium hydrogen pressure attained in a few minutes at room temperature. The heat of formation of $LaNi_5H_6$ is 7.2 kcal/mole H_2 . Assuming a formula of $LaNi_5H_{6.7}$, 100 moles of hydrogen can be stored in about 34 lbs. of alloy occupying 0.25 ft³. The sorption properties of the $LaNi_5-H_2$ system appear to be relatively insensitive to impurities in the H_2 gas, although one report¹⁷ states that small amounts (0.5%) of He or N_2 in the hydrogen can block the hydriding reaction. The alloy is not poisoned in that removing the impurity again gives the high absorption rate. Because of these desirable properties, binary metal as well as metal alloy hydrides have been proposed as media for the storage of thermal energy^{1,5,6} as well as for thermal energy conversion cycles.^{1,7-9}

Metal hydrides were proposed and are being tested¹⁰⁻¹² as off-peak energy storage systems. In this application, the large volumetric storage capacity of some metal hydrides for hydrogen is combined with the high free

energy formation of water from hydrogen and oxygen to furnish electrical power through a fuel-cell-electrolysis cycle.

The application of metal hydrides for chemical heat pump and energy conversion functions in the HYCSOS system imposes a new set of constraints on the hydride materials chosen to perform these tasks. The important parameters to be satisfied by the hydrides suitable for HYCSOS operations will become apparent in the following discussion.

III. CONCEPTUAL OPERATION OF THE ARGONNE TWO-HYDRIDE CONSERVATION OF SOLAR ENERGY SYSTEM (HYCSOS)

A schematic diagram of the initial two metal hydride concept for solar energy applications was shown and described.¹ Thermal energy, from a solar collector or reject heat, is used to decompose a hydride (M_1H) with the higher free energy of dissociation and the released hydrogen is re-absorbed at a lower temperature and stored as a second hydride (M_2H) with a lower free energy of dissociation. Pairs of hydrides with appropriate pressure-temperature relationships are available. For the initial tests of the HYCSOS demonstration unit, $CaNi_5$ is used as (M_1) and $LaNi_5$ as (M_2). Dissociation pressures and absorption pressure for $LaNi_5$ (in the middle of the plateau regions) are shown in Fig. 1.* Using a ratio of approximately .7 for the absorption pressure of the receiving metal to the desorption pressure of the decomposing hydride to obtain reasonable kinetics, the unit can be cycled between 117°C and 8°C with 40° as the intermediate temperature used for space heating.

A system of reversible metal hydrides offers the possibility of converting solar energy to electricity using three units in series. Operation in a reverse mode allows the system to be used in space conditioning and in refrigeration applications. Each of these functions will be discussed in the following sections.

* Dissociation pressure of AB_5 hydrides is a very sensitive function of B/A ratio (see section V). Pressure relationships in Fig. 1 are for $LaNi_{5.2}$ (Molycorp) and $CaNi_5$ (INCO) used in the initial series of HYCSOS tests. Since the $CaNi_5$ has essentially no hysteresis, only dissociation pressures are shown. Other data will be given in section V.

A. Thermal Energy Storage Mode

The scheme for solar energy storage and recovery is best described with reference to the schematic diagrams shown in Figs. 2 and 3. Solar energy impinging on a solar collector is picked up by heat transfer fluid circulating in the heat source loop. This fluid, at a temperature of 100 - 130°C, is pumped through the heat exchangers of two vessels filled with M_1H ($CaNiH_4$). Heat is absorbed from the fluid by M_1H which thermally decomposes to give $M_1 + H_2$. The H_2 is allowed to flow into two vessels filled with M_2 ($LaNi_5$) where it reacts to form M_2H ($LaNiH_6$). The heat of reaction is removed by fluid from the heating loop. The M_2 vessels are maintained at a temperature (say 40°C) so as to make the heat of the reaction $2M_2 + H_2 = 2M_2H$ available for space heating. The process just described simulates operation of the system during periods of insolation. In the absence of solar energy input, the flow of hydrogen is reversed, with the system now operating in a heat pump mode (Fig. 3). Fluid from the heating loop is now used to remove heat from the M_1 vessels at 40°C making the heat of the reaction $2M_1 + H_2 = 2M_1H$ available for space heating. Thermal decomposition of M_2H can occur at temperatures of approximately 8°C by absorption of heat from the outdoor ambient environment via the heat absorption loop. The hydrogen flow loops are shown above the vessels. Filters are provided in the hydrogen flow lines to prevent metal or metal hydride particulate transport in the system.

The cycle described above accomplishes solar energy thermal storage during the day and recovery at night for space heating purposes. The hydrides $CaNi_5H_4$ and $LaNi_5H_6$ have to be chosen such that their hydrogen decomposition pressures and kinetics of reaction fulfill the requirements posed by the system. Hydrogen is released from $CaNi_5H_4$ at 117°C at a pressure of ~ 10 atm and should react with $LaNi_5$ at 40°C to form $LaNi_5H_6$ (daytime operation). Hydrogen should be released from $LaNi_5H_6$ at 8°C at a pressure of ~ 1.2 atm so that it can react with $CaNi_5$ to form $CaNi_5H_4$ at 40°C where its decomposition pressure is $\sim .8$ atm (night-time operation). See Fig. 1.

B. Space Conditioning and Refrigeration Mode

The possibility of metal hydride systems, and in particular a $CaNi_5$ - $LaNi_5$ pair, to function in space conditioning and refrigeration applications is illustrated diagrammatically in Fig. 1. Using the same temperature as for

thermal storage, a reverse mode of operation for cooling purposes immediately suggests itself using this particular pair of hydrides or another pair with similar properties. This mode is shown diagrammatically in Figs. 4 and 5. In operation (see Fig. 4) heat transfer fluid from the solar collector (heat source loop) at temperatures of 117°C or higher is circulated through the first vessel containing M_1H (e.g., CaNi_5H_4) decomposing the hydride and storing the hydrogen in the third vessel containing M_2 (e.g., LaNi_5). The heat of recombination is rejected to the outdoor ambient at 40°C via the heat rejection loop. At the same time fluid from the cooling loop is circulated through vessel four. Hydrogen is released from vessel four containing M_2H (e.g., LaNi_5H_6) by absorption of heat from indoor ambient at temperatures down to 8°C . This hydrogen reacts with M_1 (e.g., CaNi_5) stored in vessel two and the heat of recombination is also rejected to outdoor ambient at 40°C via the heat rejection loop. A continuous flow of hydrogen can be maintained and therefore continuous cooling power can be provided by switching the flows of heat transfer fluid as well as the hydrogen gas flows as indicated in Fig. 5. The four unit cooling system described here is seen to be formally equivalent to the major elements of conventional absorption refrigerators.¹³

To estimate the cooling power obtainable with a CaNi_5 - LaNi_5 pair, one needs to know the heat of dissociation of LaNi_5H_6 , and the number of moles of hydrogen dissociated per unit time. Taking the heat of dissociation to be 7.2 kcal, the quantity of hydrogen to be 33 moles and a cycle time of 4 minutes gives a cooling power (down to 8°C) of ~ 4100 W. However, a small loss ($\sim 15\%$) of cooling power arises from the necessity to cool the container with LaNi_5 from 40°C to the lowest temperature in the cooling cycle.

It is of interest now to develop expressions applicable to any given pair of metal hydrides, allowing one to calculate the lowest temperature (T_3) attainable for fixed solar collector (high temperature, T_2) and reject temperatures (ambient, T_1). Let ΔH_L be the heat of dissociation of a given metal hydride with a lower heat of dissociation and therefore a higher hydrogen dissociation pressure at a given temperature than a second metal hydride with a higher heat of dissociation, ΔH_H , and therefore, a lower hydrogen dissociation pressure at the same given temperature. The entropy changes

involved in the reversible hydrogen equilibria for the hydride pair are assumed to be the same in this particular treatment. A more general treatment in which both ΔH and ΔS are allowed to vary will be given elsewhere.¹³ Beginning with the equality

$$-\frac{\Delta H_L}{T_1} + \frac{\Delta H_L}{T_3} = -\frac{\Delta H_H}{T_2} + \frac{\Delta H_H}{T_1} \quad (1)$$

one obtains after rearrangement and letting

$$\frac{\Delta H_H}{\Delta H_L} = K,$$

$$T_3 = \frac{T_1}{1 + K - \frac{T_1}{T_2} K} \quad (2)$$

$$T_2 = \frac{T_1 K}{1 + K - \frac{T_1}{T_3}} \quad (3)$$

Furthermore,

$$\Delta H_L = \Delta H_H \frac{T_2 - T_1}{T_2} \times \frac{T_3}{T_1 - T_3} \quad (4)$$

It is gratifying that this straightforward analysis gives for the heat extractable at the low temperature T_3 , the quantity ΔH_L , the heat of dissociation of the less stable metal hydride as the product

$$\Delta H_H \frac{T_2 - T_1}{T_2} \times \frac{T_3}{T_1 - T_3} .$$

Now, the quantity $\Delta H_H \frac{T_2 - T_1}{T_2}$ has been shown in a detailed analysis,³ a summary of which is given in the next section, to be the theoretical maximum

work to be derived in an energy conversion cycle involving metal hydrides. The work obtained in a conversion cycle multiplied by $\frac{T_3}{T_1 - T_3}$ is then the maximum quantity of heat extractable at the low temperature T_3 .

C. Energy Conversion Mode

The HYCSOS system also lends itself to conversion of thermal energy into useful work as electricity. The mechanical work could be used to drive the compressor of a conventional air conditioning system. Alternatively, electrical energy for home use could be generated. In the energy conversion cycle, high pressure H_2 at ~ 50 atm generated by passing 140°C fluid from the heat source loop through the first of three vessels containing M_2H , is allowed to do work in an expansion engine (see Fig. 6). The cooler, lower pressure, H_2 exiting from the expansion engine is fed into the second vessel containing M_2 where it reacts to form M_2H . (For maximum Carnot efficiency, the temperature of the reacting vessel should be kept as low as possible. However, in practice it may be desirable to generate electricity and to provide space heating at the same time. In the event, the reacting unit could be kept at 50°C at a sacrifice of conversion efficiency). After the reaction $2M_2 + H_2 = 2M_2H$ is complete in the second unit the 140°C fluid flow is directed through the heat exchanger in this vessel (Fig. 7). The high pressure H_2 produced by thermal decomposition is now fed into the third vessel containing M_2 . While the hydriding reaction is occurring in vessel three, the first storage unit is cooled to reaction temperature. By using three vessels which are alternately absorbing and desorbing hydrogen a practically constant flow of hydrogen should be maintained through the expansion engine and therefore a steady power generation should be achieved. The cycle time is determined primarily by the time needed for absorption which in turn is strongly dependent on the heat transfer from the cooling fluid to the absorbing metal powder. In cyclical fashion, one unit is always desorbing, one is absorbing, and one is in the process of heating up or cooling down.¹⁴⁻¹⁶ Three steps in the six step conversion cycle are shown diagrammatically in Figs. 6, 7 and 8.

It is of interest to consider the optimum conversion efficiency of thermal to electrical energy, which might be achieved in a HYCSOS system.

Consider the hydride system as a device which absorbs heat at the high temperature T_2 from the solar collector, and releases the heat at ambient temperature T_1 , generating an amount of work, W .

The theoretical maximum amount of work obtained from this system follows from the second law of thermodynamics and is

$$W = \Delta H_{\text{diss}} \frac{T_2 - T_1}{T_2},$$

where ΔH_{diss} is the enthalpy of dissociation of the hydride at T_2 .

The second law sets an upper limit on the amount of work that can be obtained from a heat engine operating between two specified temperatures. This upper limit can be attained only during fully reversible cyclic operation of the engine. It is well-recognized that reversibility in practical engines has to be sacrificed for increased power input so that losses of efficiency must be tolerated. Further, if it is assumed that hydrogen acts as an ideal gas, that pressure effects on the heat capacity and on the molar volumes of metal and metal hydrides can be neglected, and that the differences in molar volume of hydride and metal are insignificant, then it can be shown that ΔW is equal to $(T_2 - T_1/T_2) \cdot (\Delta H_{\text{diss}})$.² A detailed examination of the hydride conversion system shows that reversible cyclic operation is at least theoretically possible.

From a practical standpoint, the generation of electricity from the hydride conversion system requires a continuous flow of hydrogen. This can be achieved as has already been mentioned by grouping three hydride beds in a suitably staggered desorption-absorption cycle. Let the three vessels be labeled vessel 1, 2 and 3. During operation their function will be as follows. Vessel 1 absorbs heat for 4 minutes and releases 33 moles of hydrogen at high pressure. The hydrogen is absorbed by vessel 2 for the first 2 minutes, then by vessel 3. Vessel 2 is heated to the high operating temperature during the second 2 minute period. Following the desorption of hydrogen, vessel 1 is allowed to cool for 2 minutes and will then be ready for absorption of hydrogen during the subsequent 4-minute period. A similar cycle of desorption-cooling-absorption-heating applies to vessels 2 and 3 with delays

of 4 and 8 minutes, respectively, with reference to the first vessel. This staggered cycle of operations is shown schematically as Table 1.

Table 1. Basic Operational Schedule for the Conversion Cycle of the HYCSOS System Vessel

Function					
1	Desorption		Cooling	Absorption	
2	Absorption	Heating	Desorption		Cooling
3	Cooling	Absorption		Heating	Desorption
	2	4	6	8	10
Time (minutes)					

By expansion of the high pressure hydrogen through a suitable expansion engine, a certain amount of work is produced. For desorption at 140°C and absorption at 298.2 K, the maximum efficiency is

$$\epsilon = \frac{413.2 - 298.2}{413.2} = 0.28,$$

i.e., 28% of the heat absorbed by the hydrogen during dissociation can in principle be converted to electricity.

It is of interest to estimate the performance of a small scale system based on ~ 30 lbs of LaNi_5 involving a total of 33 moles by hydrogen. The dissociation pressure is given by the equation¹⁷

$$\log_{10} P_{\text{atm}} = - \frac{1587}{T} + 5.60,$$

resulting in an equilibrium dissociation pressure of 57.2 atm at 140°C, and of 1.9 atm at 25°C. In practice, the equilibrium pressure calculated using the above equation is an upper value. During desorption at 140°C the H_2 pressures are strongly composition dependent and absorption at ambient temperature will require a pressure head. It will be assumed here that hydrogen at 50 atm is available for operation of the expansion engine. The low-pressure at which absorption takes place is assumed to be 3 atm.

The heat of dissociation is 30.3 kJ/mol of hydrogen. During decomposition of 33 moles of hydrogen, therefore, 1000 kilojoules of heat have to be supplied. Assuming the expansion engine to be 90% efficient means that 33 moles of hydrogen yield 196.0 kilojoules of electricity, i.e., 19.6% of the heat supplied during desorption was converted into work. M_1 , CaNi_5 , and its hydride can also be used in the conversion mode at a reduced total pressure. Since the ratio of dissociation pressures at the same temperatures is larger than for LaNi_5 , similar conditions will yield 200.0 kilojoules of electricity. With the somewhat larger heat of dissociation, 1040 kilojoules for 33 moles of H_2 , only 19.2% is converted into work.

Under actual conditions losses will be incurred during the warming and cooling of the hydride containers. Part of the heat that has to be removed from the hot container during cooling could be recovered and used to raise the temperature of the unit to be heated next. For this purpose a buffer volume of heat exchange fluid can be cycled in a range intermediate between 25°C and 140°C, e.g., between 70 and 90°C. To cool a unit from 140°C the 70°C fluid can be circulated until a temperature near 90°C is reached. To cool the unit further, coolant can be used without heat recovery. Similarly, if a unit is to be heated subsequently, the buffer fluid at 90°C can be used to reach a temperature near 70°C. In this fashion at least part of the internal energy of the hydride containers can be cycled between the three units in a regenerative way. Such a regenerative system of heat exchangers is not explicitly shown in Figs. 6-8. The burden of unavoidable heat losses for the complete cycle is estimated to be 15% of the heat required for the dissociation of the hydride. Instead of 1000 kJ, the actual cycle would require 1150 kilojoules from the collectors. The average conversion efficiency then is estimated at 16.5%. The small scale system described above would be expected to produce 0.8 KW of electrical energy with an input of 4.8 KW of thermal energy.

IV. SYSTEM DESIGN DESCRIPTION

A. General

A demonstration test facility has been constructed, experimentally to evaluate Argonne National Laboratory's dual metal-metal hydride bed concept for thermal energy storage, mechanical/electrical power production, and

refrigeration. In this dual metal-metal hydride concept, hydrogen gas is transferred from tanks containing a metal hydride bed of one composition to tanks containing a metal hydride bed of another composition, by the action of applied thermal energy. The heat of formation of one type of hydride compound (termed M1 hydride) and sensible heats associated with system heat capacities will be supplied, at a specific temperature level which is commensurate with required system hydrogen pressure level, to decompose the M1 hydride and drive the hydrogen to the other metal (termed M2) system where the hydrogen is absorbed.

The dual metal-metal hydride demonstration unit, jointly designed by the Argonne Chemistry and Engineering Divisions, consists of four reservoirs (tanks) of approximately one-half gallon volumetric capacity each, containing two different types of metal powders or metal hydride powders. The reservoirs and hydrogen piping system are made of 316 type stainless steel. For the heat storage and refrigeration tests, two of the reservoirs contain lanthanum-nickel and/or its hydride, the other two reservoirs contain calcium nickel and/or its hydride. For the power generation tests, only three reservoirs are used containing either lanthanum-nickel or calcium-nickel.

Internal heat transfer surfaces are provided in each of the hydride bed reservoirs in the form of coiled tubing; the heat transfer cooling or heating fluid circulates inside the tubing. Safety relief valves, filters, flowmeters, shutoff valves, and manifolds between the hydride beds are provided in the hydrogen process system. The heat transfer fluid (water) is heated electrically in this demonstration system, with automatic variable power input controls, to simulate a solar heat source. Tap water is used as the heat sink in a heat exchanger system. Pressures, temperatures and flowrates are measured remotely, monitored and recorded using a digital data acquisition system.

The size of the demonstration unit was chosen as a compromise to permit large enough flow rates within the process fluids so standard flowmeters can be used, and pumping and heating power requirements are met from available laboratory supplies. Heat losses are kept to a minimum with proper insulation and by keeping heat transfer fluid volumes to a minimum. For personnel safety considerations, the hydride tanks are surrounded by a well ventilated

hood through which a large volume flowrate of air (2000 CFM) is drawn and exhausted outdoors. Continuous hydrogen concentration monitoring, with an alarm set below the flammability limit, is provided to warn of potential danger.

Design of the hydride beds internal heat exchange surface configuration, line sizes and pumping rates were dictated by design goal cycle response times. The power generation mode has the shortest characteristic design cycle time (12 minutes) which requires individual bed thermal transients to be completed in approximately 2 minutes. These times are design goals. Thermal response limitations of associated components (thermal inertia of lines, pumps, valves, and heaters), which were not considered in detail in the design analysis, are expected to degrade the achievable cycle response time of the individual hydride bed to perhaps 4 minutes. The heat storage mode and refrigeration modes of operation have design goal cycle times one-half hour and 4 to 8 minutes, respectively, so these modes are not design limiting. It will be seen that in the initial operations design cycle times are approached.

B. Heat Transfer Fluid System

Three fluid heat transfer loops, Fig. 9, are available and can be remotely valved and pumped to the appropriate tanks. The solar or other suitable low temperature thermal energy input, loop A, is simulated by an 18 KW electric heater. Loop B, a water cooled heat exchanger of 25 KW heat transfer capacity, represents the space being heated in winter and serves for ambient heat rejection during cooling cycles. A heat exchanger cooling water circuit is provided from the building water supply. A third fluid loop, loop C, with a 6 KW electric heater is the refrigeration heat load in the cooling cycle and the ambient heat supply during the recovery cycle.

The heat transfer system, Fig. 10, contains water in all three heat transfer fluid loops. The valves which control the flow of water through the hydride tank heat exchangers are double acting air actuators controlled by solenoid operated air valves. The water plumbing system is 3/4 inch x .065 wall hard copper tubing with soft-soldered (50/50 type) socket joint fittings.

Each flow loop incorporates a one gallon fluid expansion and surge tank of type 304 stainless steel and rated for 400 psig operation. Each surge tank has a sight gauge to show liquid level, nitrogen pressurization valve, a relief valve and a water fill valve.

The heating loop "A" has three electric heater assemblies for heating the water. These heaters, arranged in parallel flow, consist of a 240 VAC Watlow "Firerod" cartridge heating element 5 feet long of 6 KW capacity encased within 1 1/8 inch OD type K hard copper tubing. The heat transfer fluid outlet is in line with the axis of the assembly at the opposite end from the inlet.

A bypass throttling valve (VTA), is used to manually vary the flow rate of heat transfer fluid through the hydride beds. Flow loop A incorporates a bypass relief valve to protect the pump in the event that all inlet valves are closed. A manual bronze ball valve is incorporated at the low point in the loop to drain the system. The pump is a turbine type rated at 6.2 gpm at 65 psid, and is driven by a 1/2 hp electric motor.

Cooling loop "B" features a water to water heat exchanger for cooling the recirculated process fluid. Tap water from a 1 1/2 inch, 60 psig laboratory supply is used to cool loop B fluid. The water pump is a turbine type having a rating of 12.4 gpm at 65 psid and using a 1 1/2 hp electric motor drive. The loop has a water bypass relief valve (VBB) and a throttling bypass valve (VTB).

The water pump for the water cooling loop associated with loop B is also a turbine type. Two bypass flow loops around the water pump are provided. One with a pressure relief valve to protect the pump in case of operator error and the second bypass loop allows for adjustment of the water sink temperature in the heat exchanger, and the consequent heat exchanger heat load capacity, by manual adjustment of throttling valves.

The refrigeration loop "C" features a single electric heater of 6 KW capacity, which serves as the equivalent heat load of this circuit. The turbine type pump is rated at 6.2 gpm at 65 psid and is driven by a 1/2 hp electric motor. Detailed fluid system requirements are shown for each circuit.

Table 2. Heat Transfer Fluid Loop A

Maximum Fluid Temperature	135°C (275°F)
Design Temperature Range	21°-135°C (70-275°F)
Design Pressure (max)	100 psig
Relief Pressure	110 psig
Static Pressure	40 psig
Pump Pressure (Head)	60 psid
Flow Rate (max)	6 gpm
Heat Transfer Fluid	water
Power Input (Heating)	0-18 KW
Heater Voltage	0-208 (3 ϕ) VAC
Pump Power	0.50 hp

Table 3. Heat Transfer Fluid Loop B

Primary Loop

Maximum Fluid Temperature	61°C (142°F)
Design Temperature Range	25-50°C (77-122°F)
Design Pressure (max)	100 psig
Relief Pressure	110 psig
Static Pressure	40 psig
Pump Pressure (Head)	60 psid
Flow Rate	12 gpm
Heat Transfer Fluid	water
Heat Transfer Capacity	25 KW (70°F sink, 122°F source)
Pump Power	1.5 hp

Heat Exchanger Cooling Water Circuit

Maximum Temperature	21°C (70°F)
Design Pressure	120 psig
Static Pressure	60 psig
Pump Pressure (Head)	60 psid
Flow Rate (max)	6 gpm
Heat Transfer Capacity	25 KW (70°F/21°C sink, 122°F/50°C source)
Pump Power	0.50 hp

Table 4. Heat Transfer Loop C

Maximum Temperature	61°C (142°F)
Design Temperature Range	- 31° to 21°C (-24 to 70°F)
Design Pressure (max)	100 psig
Relief Pressure	110 psig
Static Pressure	40 psig
Pump Pressure (Head)	60 psid
Flow Rate (max)	6 gpm
Heat Transfer Fluid	water
Power Input (Heating)	0-6 KW
Heater Voltage	0-208 (3 ϕ) VAC
Pump Power	0.50 hp

C. Hydrogen System

The hydrogen system consists of hydride tanks with internal heat exchangers, piping and valving as shown in Fig. 11.

Four metal/metal-hydride filled tanks are used in the demonstration system as shown in the system layout. Each of these tanks is constructed as shown in Fig. 12. The tank cylindrical wall is a 9 1/4 inch length of 4 inch SCH 10 type 316L stainless steel pipe. The tank heads are 4 inch SCH 10-IPS type 316L stainless steel pipe caps. Stainless steel tabs are welded to the side of the cylinder for mounting the tank in a vertical orientation.

A number of coils of tubing form a heat exchanger inside of each hydride tank as shown in Figs. 12-14. External shaped tubing cooling/heating coils attach to the outside of each tank. Internal manifolding for the cooling/heating coils is provided by a Tee shaped tubular assembly which connects to the outlet manifold head as shown in Fig. 12.

Each tank was constructed so that all pressure boundary welds were 100% radiographed and dye penetrant checked. The tanks were hydrostatically tested to 1000 psig. Each tank was constructed with the top hydrogen outlet and the bottom water-glycol inlet and outlets having compression type fittings such that any of the tanks can be readily removed from the system for changing hydride material. The hydride material which fills each tank approximately 2/3 full is poured in or out through the top hydrogen line.

A hydrogen filter, Fig. 15, is incorporated immediately above the hydride tank to preclude transfer of hydride through the lines into the valves, which could cause leakage, and to preclude contamination of the other type hydride material. The cylindrical pressure shells are 2 inch Sch 10 type 316 stainless steel pipe containing a cylindrical porous sintered 316 stainless steel filter element having 0.25 sq. ft. surface and a 1 micron absolute filtration retention. All pressure boundary welds were 100% radiograph and dye penetrant tested. The filters were hydrostatically tested to 1000 psig.

The hydrogen piping between each hydride tank and its filter is 1/2 inch diameter type 316 stainless steel tubing having .049 inch wall thickness. Above the filters, all of the hydrogen lines are 3/8 inch diameter type 316 stainless steel tubing having .035 inch wall thickness. The tubing sections and components in the hydrogen flow system are connected together using Swagelok fittings. See Fig. 11.

The remote actuated hydrogen valves are nominal 3/8 inch bellows sealed type 316 stainless steel valves with air to open, spring closed actuators. The manual hydrogen valves for filling and venting the hydrogen system and the relief valves are also 3/8 inch bellows sealed type 316 stainless steel. Design requirements for the hydrogen system are shown in Table V.

Table 5. Hydrogen System

Hydrogen Loop

Design Pressure (max)	750 psig
Design Pressure (min)	30 psig
Relief Pressure	825 psig
Design Temperature (max)	135°C (275°F)
Design Temperature (min)	-31°C (-24°F)
Hydrogen Flow Rate (max)	0.55 gm/sec
The hydrogen shall be filtered to 1 micron absolute size at the outlet of each hydride tank.	

Hydride Tanks

Design Pressure (max)	750 psig
Design Pressure (min)	30 psig
Relief Pressure	825 psig
Design Temperature (max)	135°C (275°F)
Design Temperature (min)	-31°C (-24°F)
Free Internal Volume	2.5 liters
Hydride Volume	1 to 1.5 liters/tank

D Hydrogen System Instrumentation

The instrumentation and control functions which are required for operation of the demonstration unit, for the most part, are remote for the experimental apparatus to reduce operator exposure to potential hazards. Air operated remote valves in the hydrogen system were specified to eliminate spark and explosion potential.

Flow from each hydride tank is measured using a Brooks heated tube mass flowmeter. Remote recording of flow rate and integrated flow is done with the digital data logger. Remote readout is on a graphic display panel, Fig. 16. The hydrogen flowmeters are located on the "clean side" of the filters to minimize contamination from the fine hydride particles. Four hydrogen flowmeters are provided.

Hydrogen absolute pressure level is monitored at a position in the system immediately above the filter (on the clean side) using Sensotec metal diaphragm, type transducers rated from 0 to 1000 psia. Four hydrogen pressure transducers are provided. The pressure drop through the filter during hydrogen flow conditions is accepted as a known system error for initial phases of operation. Temperature of the hydrogen is monitored at a position above each filter using immersion type copper/constantan thermocouples inserted into the flow stream. Temperatures are recorded on the digital data logger which provides automatic reference temperature compensation.

E. Heat Transfer Fluid Transport System Instrumentation

Temperatures of the water heat transfer fluid and water coolant are measured using immersion type copper constantan thermocouples and are recorded on the digital data logger. Heat transfer fluid temperatures are measured at the inlet and outlet of each of the four hydride beds (e.g., T1A1 and T1A2 for bed HT1; see Fig. 9). In heating loop A, heat transfer fluid temperatures are measured at the inlet and outlet of the electric heater (TA1 and TA4). In cooling loop B, heat transfer fluid temperatures are measured at the inlet and outlet of the heat exchanger (TB1 and TB2). In the water cooling circuit, the temperature of the supply water (TW1) and the temperatures of the water at the inlet and outlet of the heat exchanger (TW2 and TW3) are measured. In refrigeration loop C, the temperatures of the heat

transfer fluid at the inlet and outlet of the electric heater (TC1 and TC4) are measured.

Heat transfer fluid flowrates are measured at the inlet to each hydride bed heat exchanger (e.g., FIAB), using turbine flowmeter. The signal from each of these flowmeters is recorded by the digital data logger and also displayed on the remote graphic panel (Fig. 16). The bypass flows of heat transfer fluid in loops A, B, and C and the recirculation flow of water in the water cooling circuit are measured locally with Rotameters. Water flow through heat exchanger (HXB) is measured using a turbine flowmeter and is recorded on the digital data logger and displayed on the remote graphic display panel.

Pressure levels in the heat transfer fluid flow circuits are measured with local indicating gauges. The gas pressure above each surge tank (in loops A, B, and C), the heat transfer fluid pressure on the downstream side of the pump in each circuit (loops A, B, and C) and the laboratory water supply pressure are measured locally.

F. Fluid Transport System Controls

The valves which control the water heat transfer fluid flow through the hydride bed heat exchangers are air actuated solenoid valves. Sets of solenoid valves associated with a given hydride tank are controlled by a single switch to prevent a tank from being simultaneously open to more than one fluid loop. The bypass throttle valves (VTA, VTB, and VTC) in loops A, B, and C, which control the net flowrate of heat transfer fluid through the hydride bed heat exchangers, and the water supply valve are manually operated.

The electrical heater for the heat transfer fluid in loop A can be controlled from the graphic panel (Fig. 16), in either a constant power mode or in a constant output fluid temperature mode of operation. Power level or fluid temperature level is adjustable from the remote control panel. The constant temperature mode of operation for the heater in loop A operates with feedback control of temperature as monitored by thermocouple TA2 located downstream of the heater. The fluid heater for loop A has an interlock to shut off power when flow through the system is below a set level as determined by

flowswitch (FSA). If the set heater outlet fluid temperature is exceeded or the power to pump PA is lost, a safety interlock shuts off the heater power.

An identical electrical heater control system is provided for flow loop C. Thermocouple TC2 controls output fluid temperature via heater control HC. Overtemperature of the output fluid is precluded via interlock (HC) using thermocouple TC3. Flow switch FSC shuts off the heater power if the flow rate is too low. The pump (PC) must be energized before the heater can be energized. Controls for the two aforementioned heater and pump functions are mounted on the remote panel along with indicators of the specific functions (i.e., status lights and panel meters for set point temperatures and power levels). Flow loop B and the water coolant recirculation pump have an on-off switch for pump power. The energy usage for each heater and pump is recorded by the data logger. Heater powers are displayed on the graphic panel.

G. Data Logger

The short HYCSOS cycle times necessitate an automatic data logger to record all of the pertinent system variables for analysis. The data logger used is a John Fluke Mfg. Co. Model 2240 A with 30 wide range voltage input channels, and 15 alarm limits. The data logger currently samples input data at the rate of three channels/second and prints output information on paper tape.

H. Hydrogen Safety

Because of the wide explosive and flammability limits of air-hydrogen mixtures, the hydrogen containing system is housed in a well ventilated enclosed structure, Fig. 11, with an air flow of 2000 CFM. This flow is sufficient to maintain the hydrogen concentration below the 4 volume percent flammable limit in a maximum credible accident, the release of the total 43 SCF of hydrogen during the two minute thermal transient excursion of the energy conversion mode. The sloping top of the enclosing and continuous hydrogen concentration monitoring prevent unknown accumulation of hydrogen. Limit pressure alarms on each tank warn of potential hydrogen buildup in the tanks. Pressure relief valves on each tank are set 10% below the design pressure limit.

V. HYDRIDE MATERIALS

The Argonne HYCSOS concept requires pairs of hydrides having pressure-temperature relationships which permit reversible hydrogen transfer at appropriate temperatures. See Fig. 1. Alloys of the form AB_5 are eminently suitable for this purpose. See section II. By varying the materials A and B and the ratio B/A, pressure-temperature relationships over wide ranges are obtainable. The alloy $LaNi_5$ has a region of homogeneity extending from $LaNi_{4.9}$ to $LaNi_{5.4}$ with a three-fold change in plateau dissociation pressure as given by $\ln p = 2.4X - 10.75$ at $40^\circ C$ where X is the $[B]/[A]$ ratio.¹⁸ Desorption isotherms at 40° for the homogeneity region are shown in Fig. 17. Discrepancies in values of dissociation pressure of different samples are likely due to variation in alloy composition. Inhomogeneous samples, with a range of compositions, will exhibit sloping plateau pressures. Typical absorption-desorption isotherms for $LaNi_5$ hydride, Fig. 18, show the hysteresis effect in this alloy.¹⁷ Large hysteresis effects can render alloys unsuitable for HYCSOS operation. Although believed due to internal stresses on hydride formation, hysteresis effects are poorly understood and can vary with conditions of preparation. Figure 19 shows hysteresis effects in different preparations of $NdNi_5$.¹⁹ Because it can not be consistently prepared with low hysteresis, $NdNi_5$ was not an initial candidate for HYCSOS testing as M_2H , the less stable member of a hydride pair.

Although relatively inexpensive and potentially usable as M_2H , mish-metal nickel hydride with a dissociation pressure of approximately 20 atmospheres at room temperature is unsatisfactory because of its very large hysteresis. Mish-metal is a natural mixture of rare earth elements of approximate composition Ce - 50%, La - 30%, Nd - 14%, Pr - 4% and other rare earths the remaining 2%. The large hysteresis is apparently due to the high cerium content. Cerium-free mish-metal nickel hydride with a reported room temperature dissociation pressure of 4-5 atm, and small hysteresis is a good candidate.

Calcium nickel hydride, whose alloy was obtained from the International Nickel Company, has properties, Fig. 20 and Fig. 1, which make it suitable for the initial HYCSOS tests.

Under contract to the Argonne National Laboratory to develop a low hysteresis alloy usable as a stable hydride, M_2H , with $LaNi_5$, the Denver Research Institute of the University of Denver prepared samples of $La_{1.02}Ni_{4.6}Mn_{0.37}$ alloy. Figures 21 and 22 show desorption isotherms and a calculated heat of formation for this alloy. The use of ternary alloys make available a large number of potential candidates for use in the HYCSOS system.

VI. RESULTS AND DISCUSSION

In order to evaluate heat balances in the various hydriding and dehydriding cycles, it is necessary to know base-line thermal characteristics of the HYCSOS system. Using measured integrated heater power inputs, preliminary heat capacity values have been determined for empty uninsulated portions as follows:

Heater Loop A+ Tank 2 = 7.1 kcal/deg.

Heater Loop C+ Tank 3 = 1.9 kcal/deg.

The heat equivalent of the pump power input under typical operating conditions is about 200 watt hours, sufficient to raise the heat transfer fluid in the uninsulated loop by approximately 25°C. These and other measurements will be re-run on the insulated system.

Because of ready availability in sufficient quantity, $CaNi_5$ and $LaNi_5$ have been used in the first series of tests. Five kilograms (11.561 moles) of $LaNi_5$ (Molycorp.) was put through a #12 sieve (1.68 mm) and added to tank 3 through the hydrogen gas tube. Approximately half the charge was fine powder obtained by ballmilling oversize pieces. An equivalent hydrogen capacity amount of sieved $CaNi_5$, 5.8 Kg (17.341 moles), (Novamet Corp., International Nickel Co.) was added to tank 2. Determination of the bulk density by reduction of gas volume in the tanks after addition of the alloys, 8.9 gm/cc for $LaNi_5$ and 6.9 gm/cc for $CaNi_5$, compares favorably with the crystal density measurements of 8.3 gm/cc for $LaNi_5$ and 6.7 gm/cc for $CaNi_5$.

Approximately thirty seven moles of ultra high purity hydrogen (Matheson, 99.999%) were added in five to ten mole batches at 600 PSI to initially hydride and activate the $LaNi_5$. The final composition was $LaNi_5H_{6.10}$ at 16.3°C and 124 psi. Hydrogen to activate the $CaNi_5$ was transferred from the $LaNi_5H_{6.1}$ at 78°C to the $CaNi_5$ at 12°C to form $CaNi_5H_{3.4}$ at 21.7 psi leaving

$\text{LaNi}_5\text{H}_{1.74}$ as the residual composition of the LaNi_5 hydride. Calcium nickel hydride was decomposed in the storage mode by circulating water at 100°C through its bed and absorbing the hydrogen on the LaNi_5 , cooled to remove the heat of hydride formation. Typical data collected on the data logger for the storage mode is shown in Fig. 23. Figure 24 is a linear plot of the integrated power required to maintain the temperature of the dissociating CaNi_5 hydride at a relatively constant 100°C . The intercept of the extrapolation to the vertical axis, the start of hydrogen transfer, is the energy actually used to decompose the $\text{CaNi}_5\text{H}_{3.66}$ and give up approximately 25 moles of H_2 . The determined value, 0.225 KWH, gives a calculated heat of dissociation of CaNi_5H_4 of 7.7 kcal/mole H_2 , to be compared with a literature value of 7.5 kcal/mole H_2 . A typical recovery mode is shown in Fig. 25.

A summary of the data obtained in three cycles in the storage mode, the high temperature decomposition of CaNi_5 hydride and formation of LaNi_5 hydride and three cycles in the recovery mode, the low temperature decomposition of LaNi_5 hydride and formation of CaNi_5 hydride are shown in Table VI and Table VII, respectively. The data represent the first 15 minutes of a 45 minute cycle when 75%-90% of the hydrogen was transferred. ΔH_p is the heat of formation or decomposition for the amount of hydrogen involved expressed as a positive quantity. The heat recovered or heat added is the product of the temperature difference across the appropriate tank, taken at one minute intervals, and the fluid flow during that interval. The initial hydrogen flow when the valve was first opened was so large as to exceed the instrumentation limits and may also account for loss in heat measurements in the first minute interval. Except for the high temperature dissociation of CaNi_5 hydride, no attempt was made in these preliminary experiments to maintain isothermal conditions and together with heat loss in the initial interval measurement could account for the incomplete heat balances. The temperature rise of the decomposing LaNi_5 hydride after seven minutes, Fig. 25, is due to heat input from the pump.

All of the runs up to now have been made in the absence of insulation. The next phase of operation will be to determine heat balances and cycle times with thermal insulation in place.

It can be concluded that the system is meeting design specifications and that the scientific feasibility of the HYCSOS concept has been demonstrated.

Table 6. Storage Mode Hydrogen Transfer: CaNi_5 Hydride to LaNi_5

Run	H_2 Moles	<u>CaNi_5 HYDRIDE</u>			<u>LaNi_5 HYDRIDE</u>		
		ΔH_B kcal	Heat added kcal	Heat Add. $\frac{\Delta\text{H}_\text{B}}{\%}$	ΔH_B kcal	Heat Recovered kcal	Heat Rec. $\frac{\Delta\text{H}_\text{B}}{\%}$
6	20.65	154.88	177.20	115	148.68	135.03	91
8	22.59	169.42	203.36	120	162.65	122.66	75
10	21.09	158.18	164.60	104	151.85	124.22	82

Table 7. Recovery Mode Hydrogen Transfer: LaNi_5 Hydride to CaNi_5

Run	H_2 Moles	<u>CaNi_5 HYDRIDE</u>			<u>LaNi_5 HYDRIDE</u>		
		ΔH_B kcal	Heat Recovered kcal	Heat Rec. $\frac{\Delta\text{H}_\text{B}}{\%}$	ΔH_B kcal	Heat Added kcal	Heat Add. $\frac{\Delta\text{H}_\text{B}}{\%}$
7	23.36	175.20	149.75	85	168.19	119.09	71
9	18.10	135.75	137.22	101	130.32	97.04	74
11	21.91	164.32	164.30	100	157.75	122.35	76

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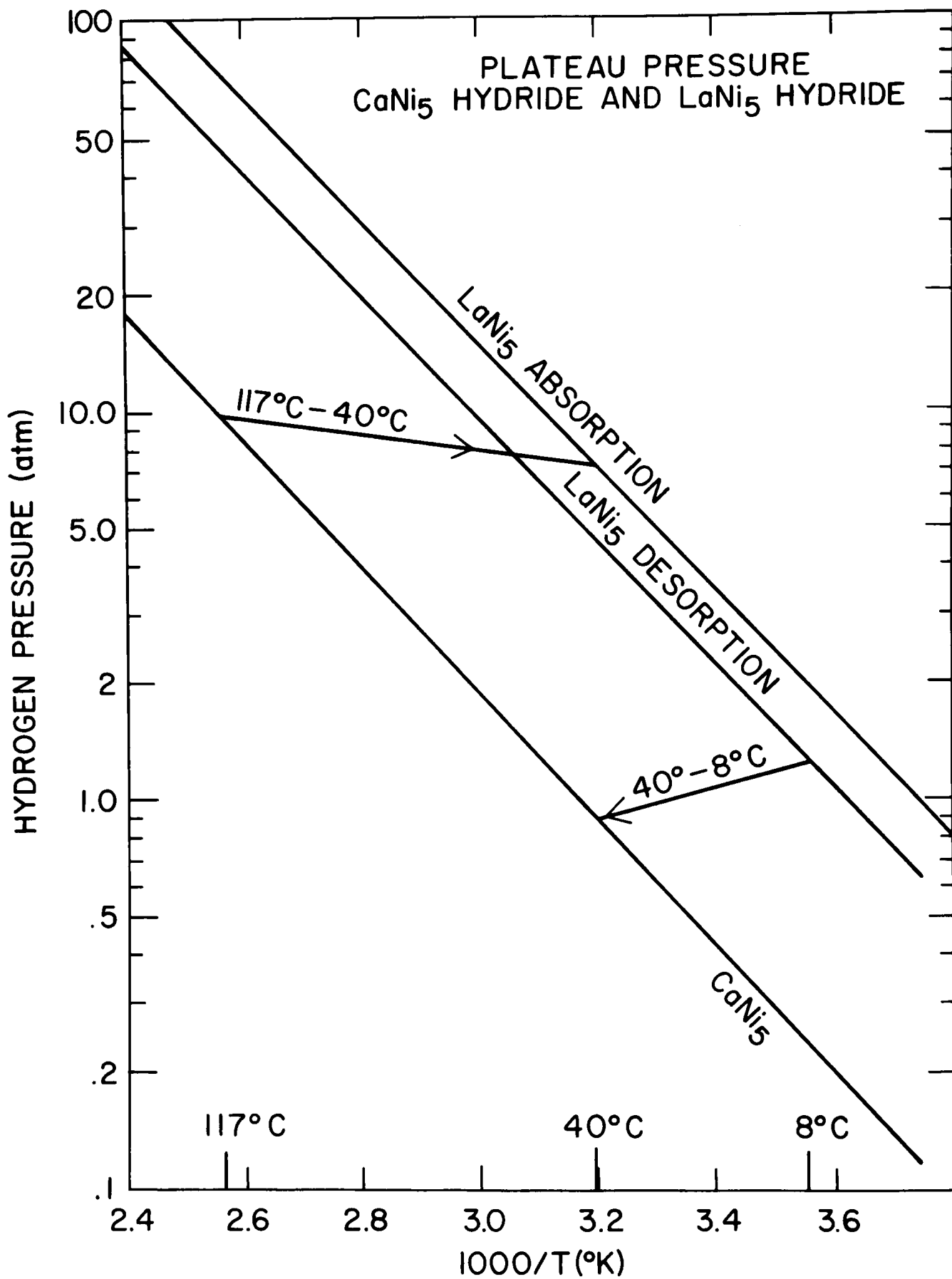


Fig. 1

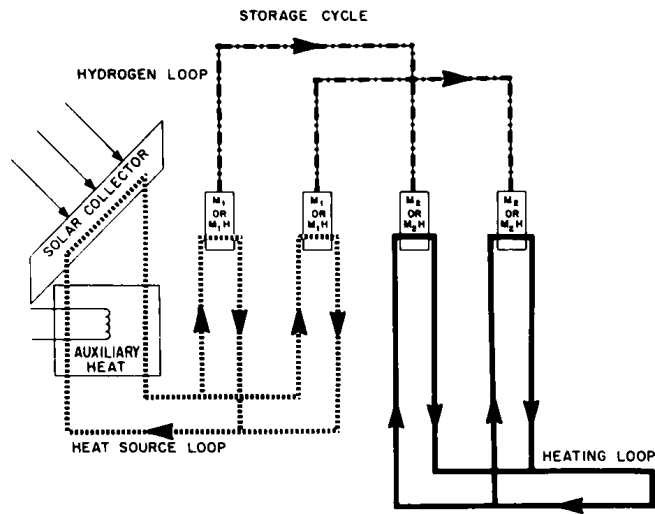


Fig. 2

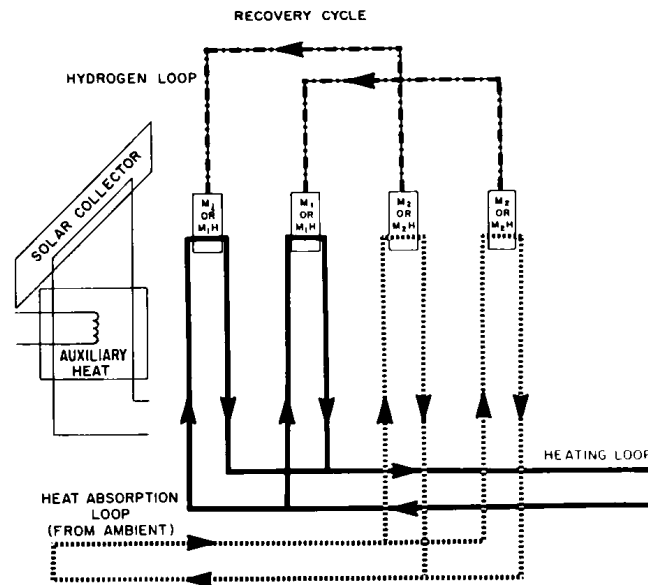


Fig. 3

Thermal Storage and Recovery Cycle

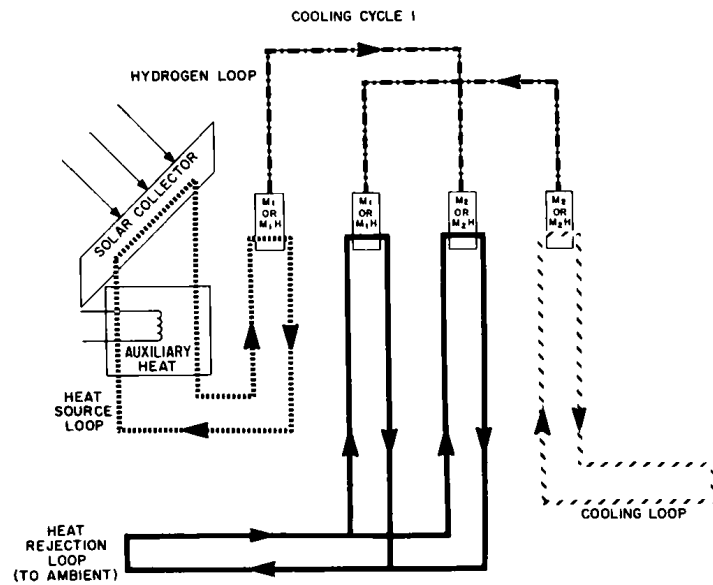


Fig. 4

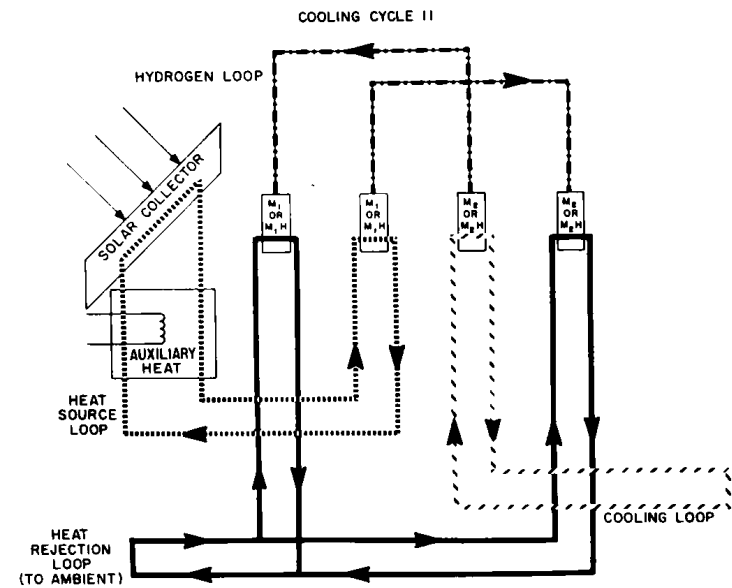


Fig. 5

Cooling Cycle

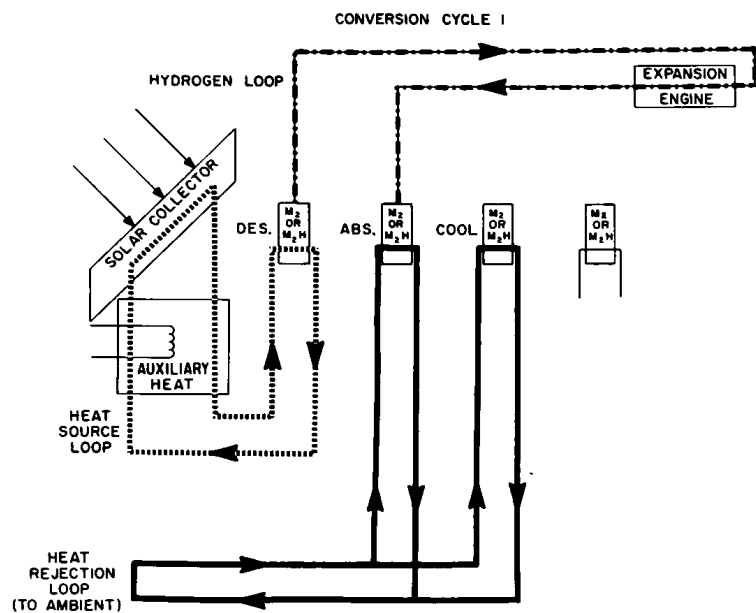


Fig. 6

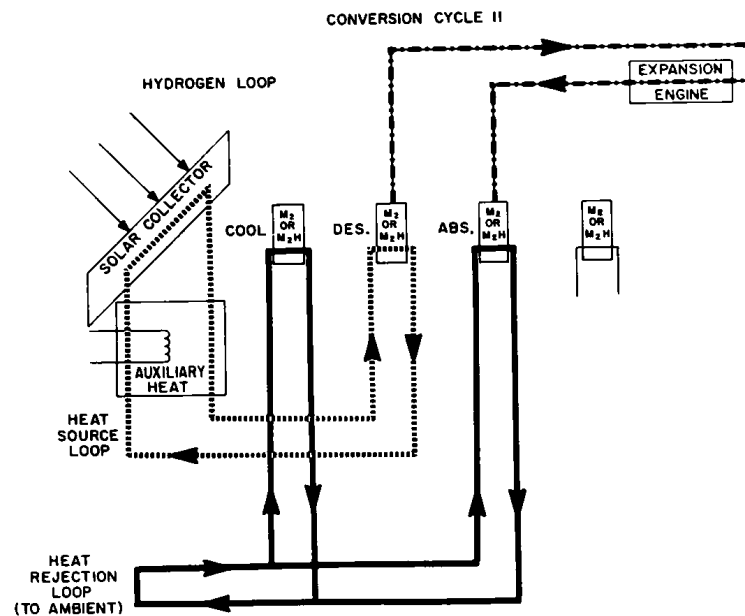


Fig. 7

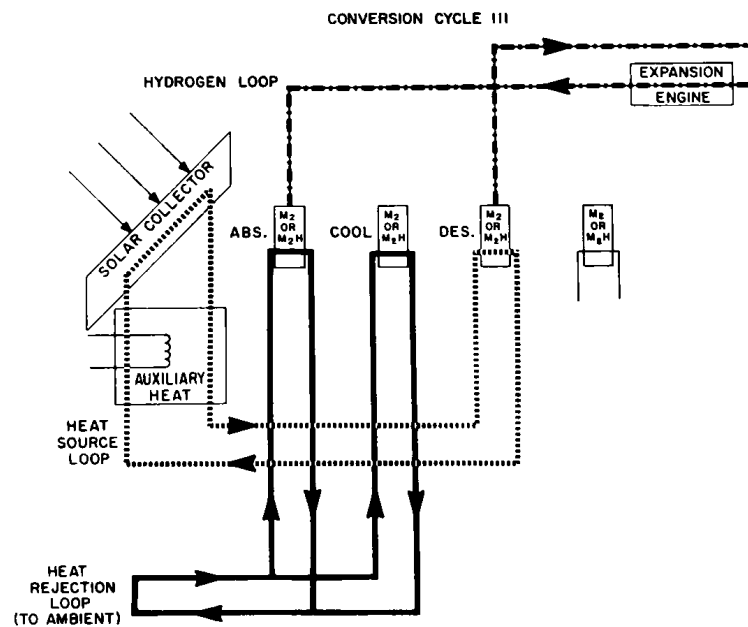


Fig. 8

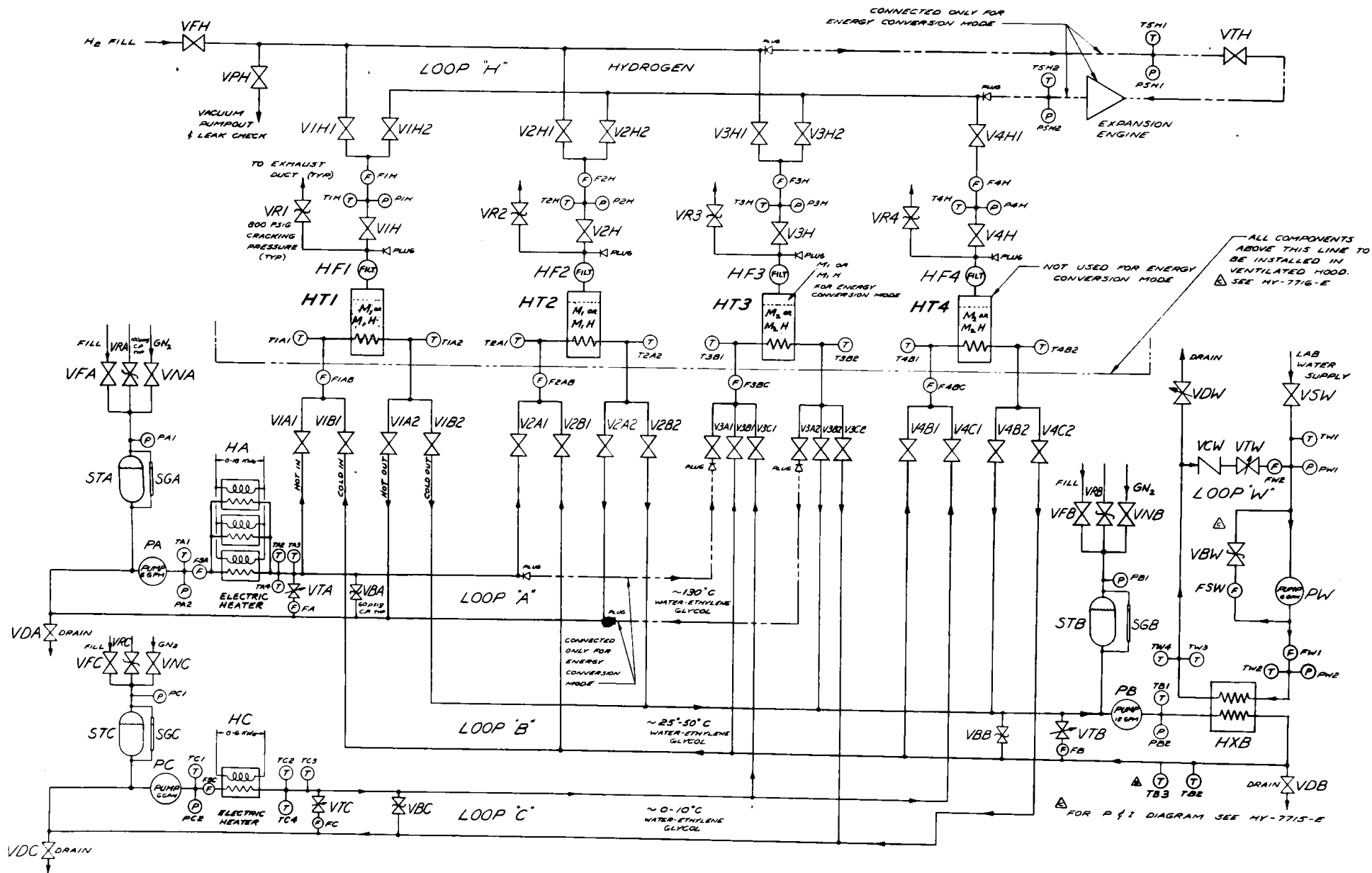


Fig. 9. HYCSOS System Layout

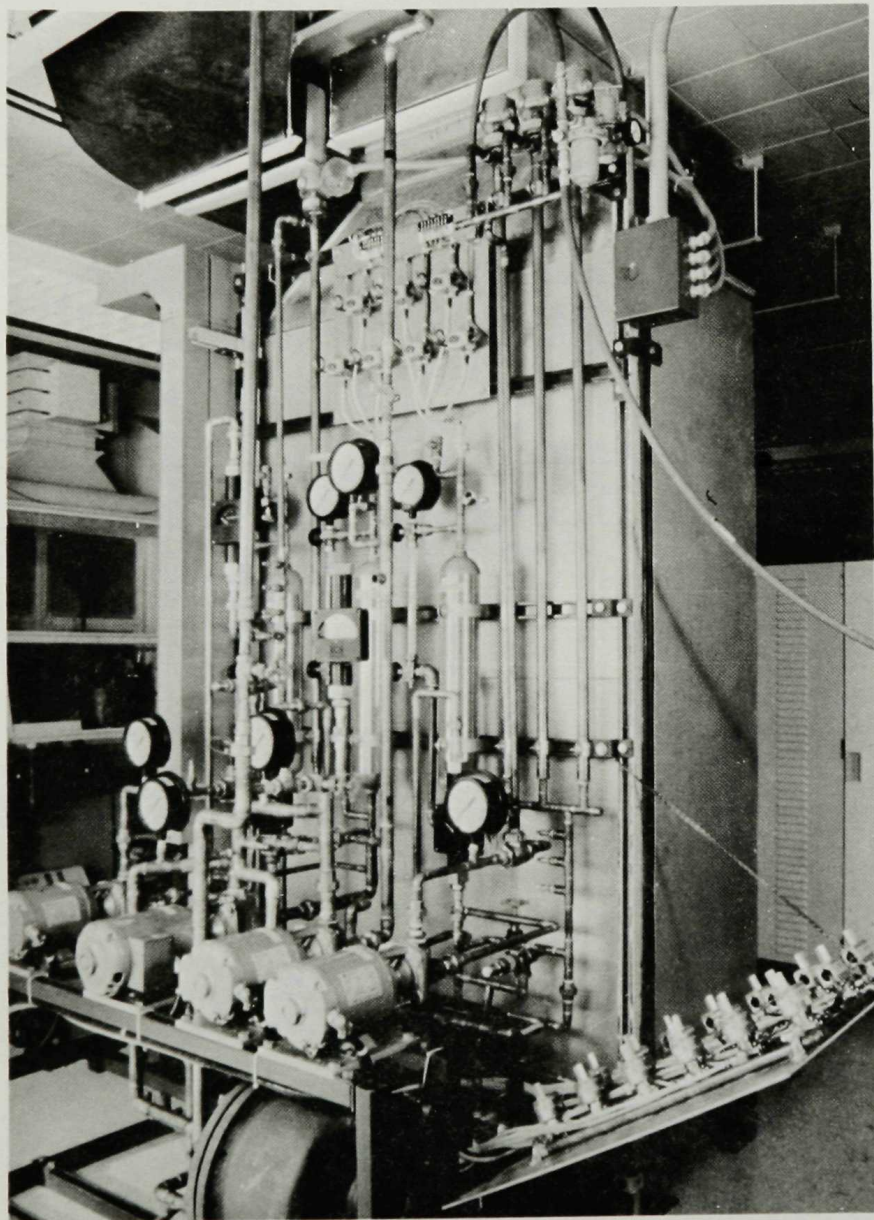


Fig. 10. Heat Transfer System

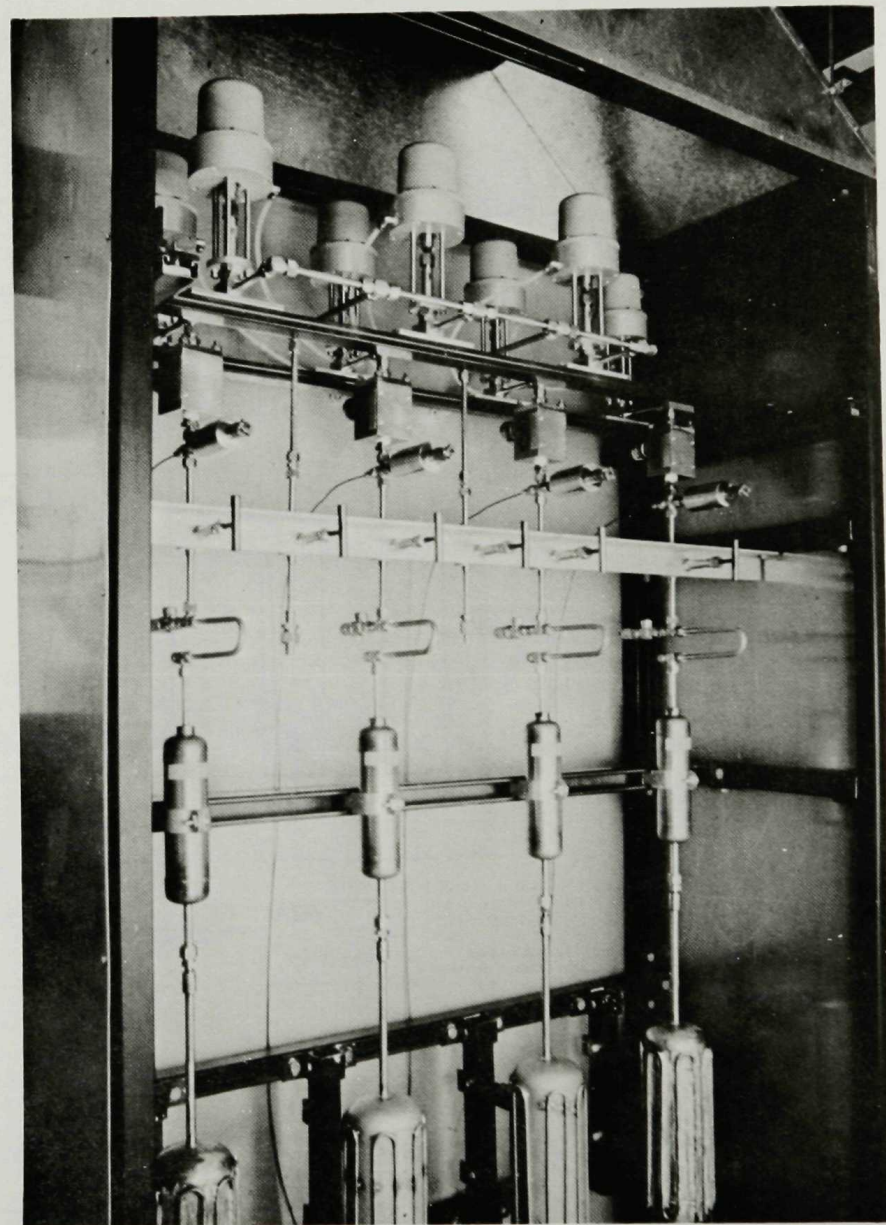


Fig. 11. Hydrogen System

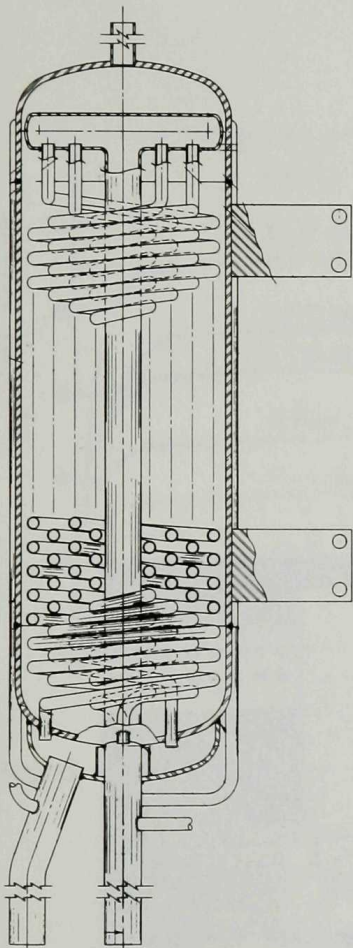


Fig. 12



Fig. 13

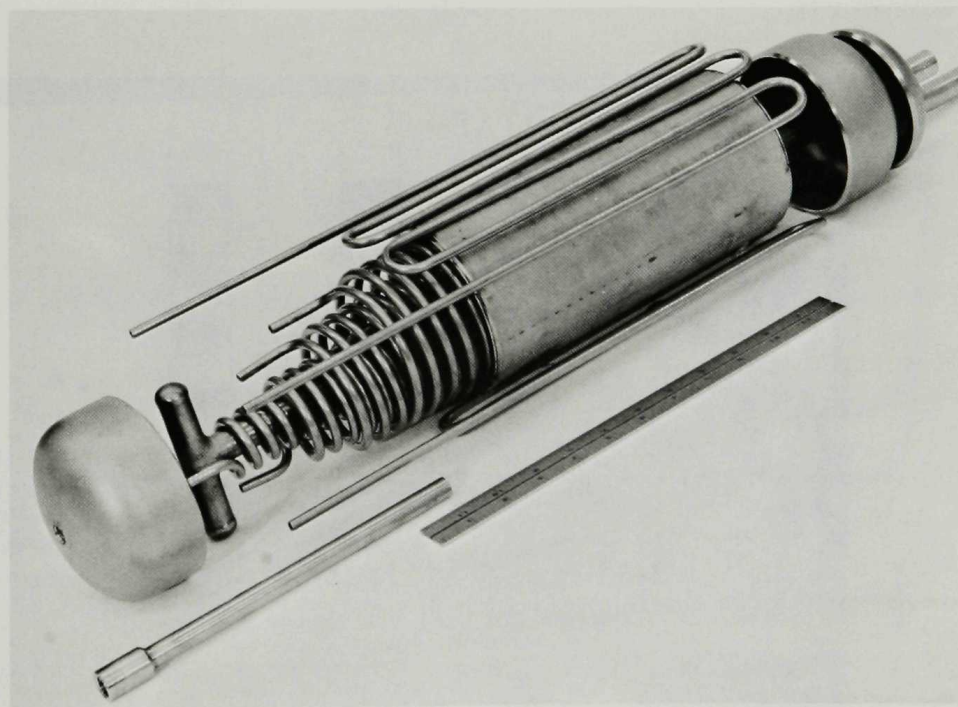


Fig. 14

Hydride Tank Construction

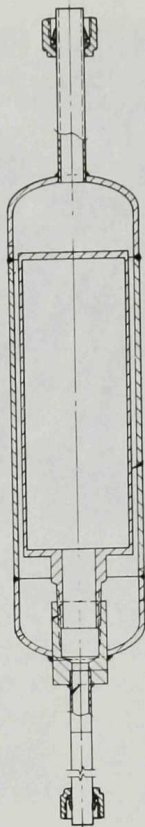


Fig. 15
Hydrogen Filter

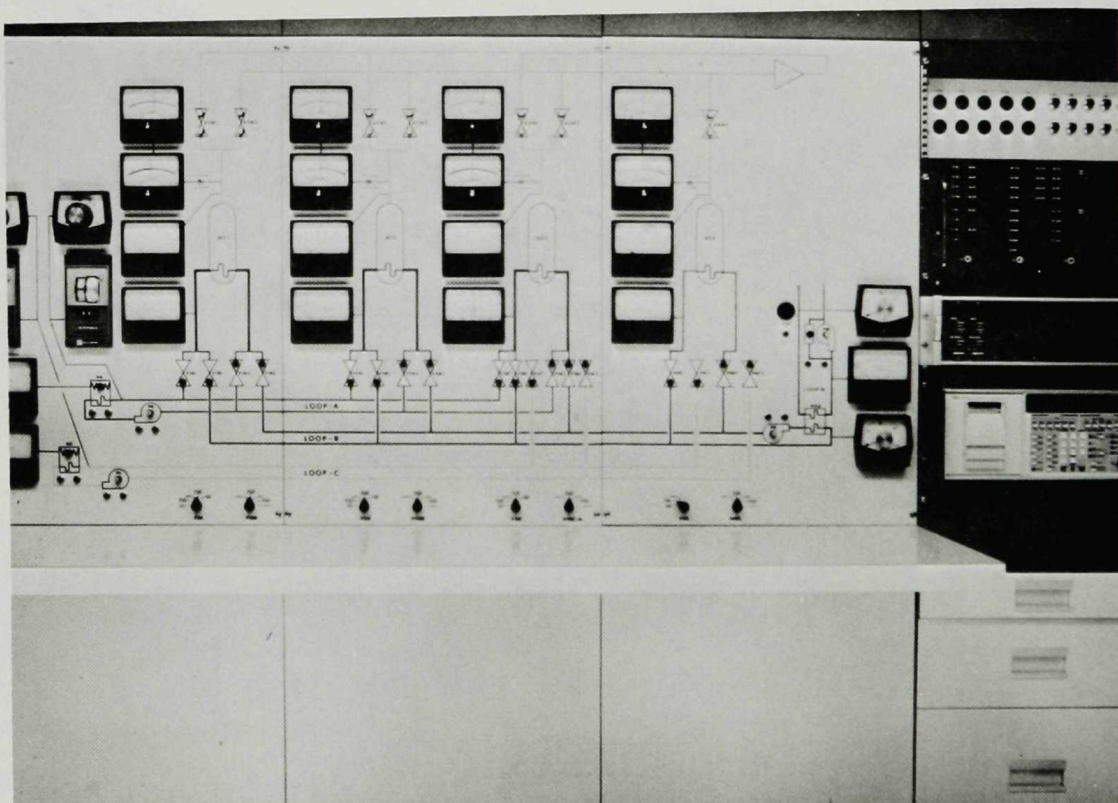


Fig. 16. Graphic Panel

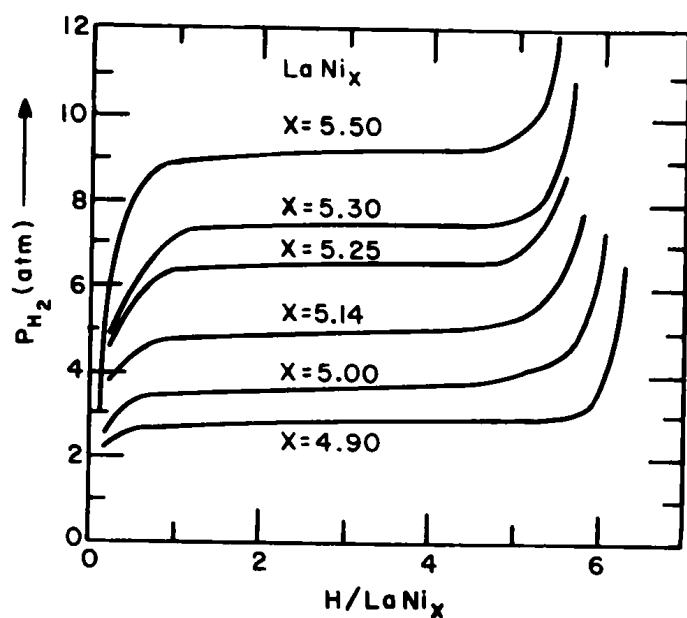


Fig. 17 Desorption isotherms at 40°C for the homogeneity region of the LaNi_x phase.

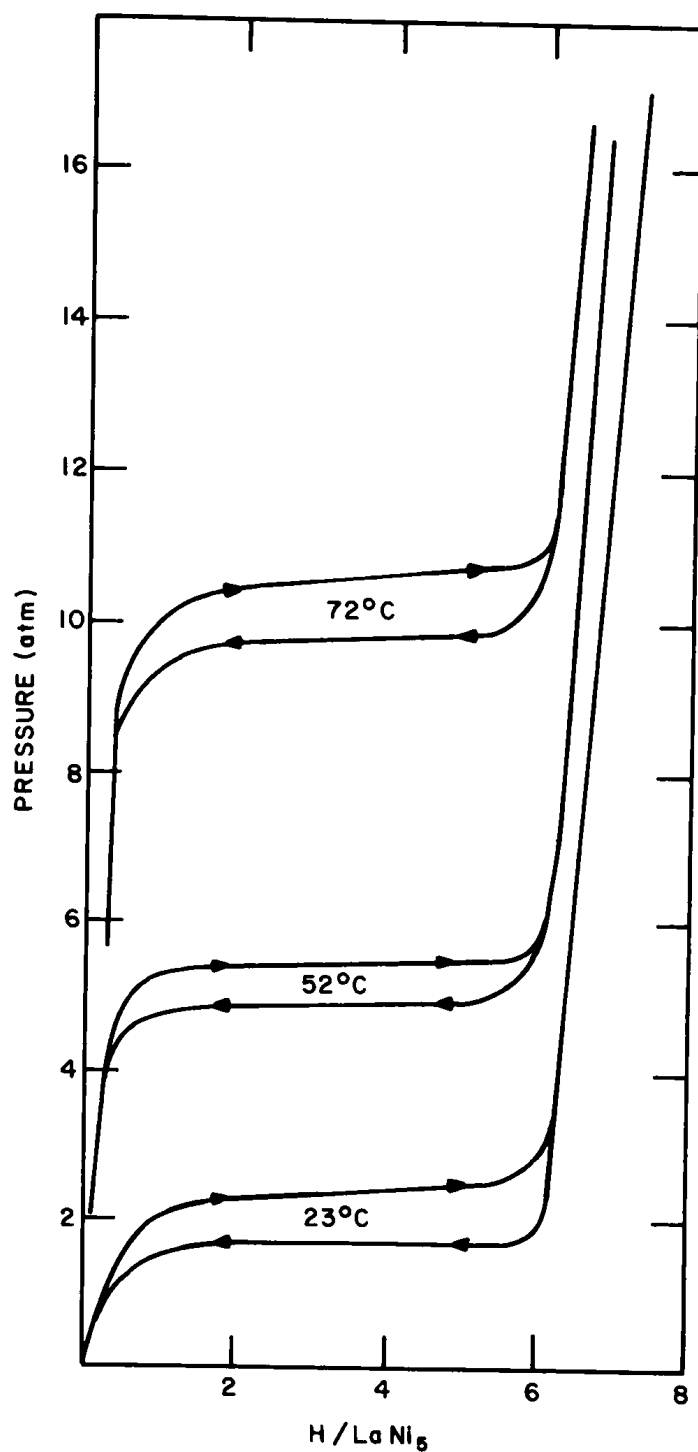


Fig. 18 Absorption-desorption isotherm for $\text{LaNi}_5 + \text{H}_2$.

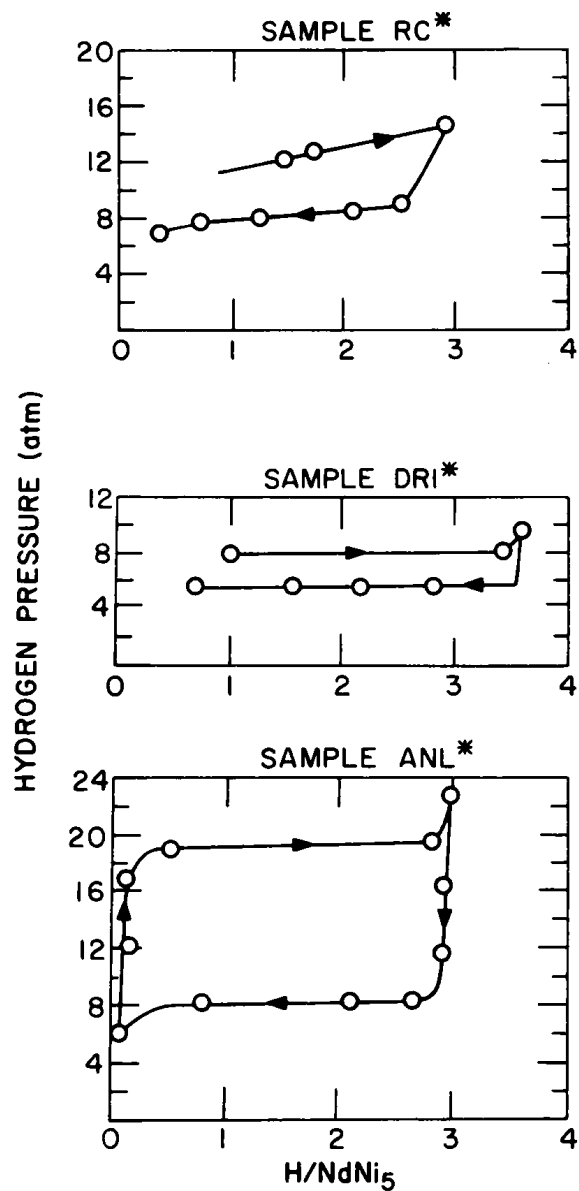


Fig. 19 HYSTERESIS IN $NdNi_5$ AT $0^\circ C$

* RC: RESEARCH CHEMICAL CO.
 DRI: DENVER RESEARCH INSTITUTE
 ANL: ARGONNE NATIONAL LABORATORY

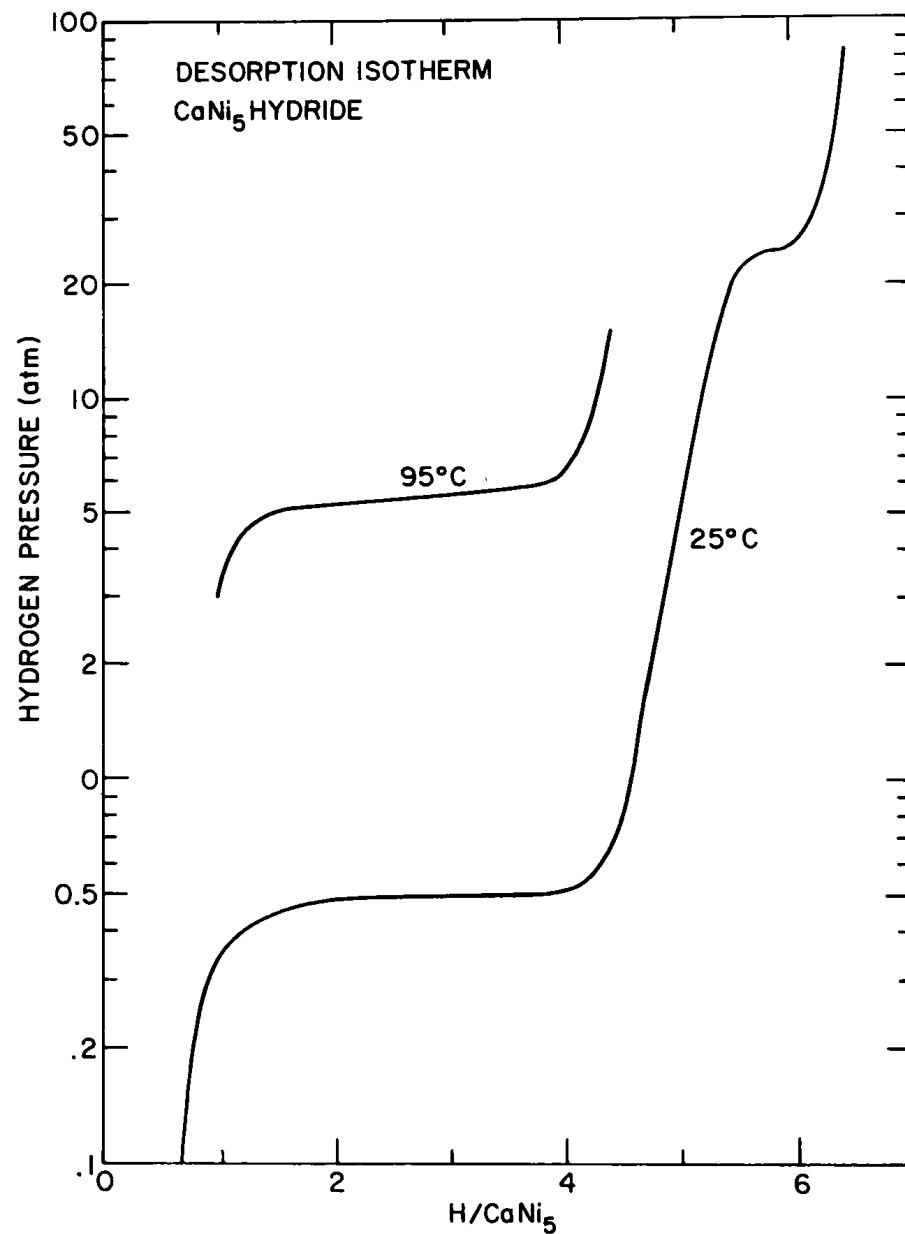


FIGURE 20

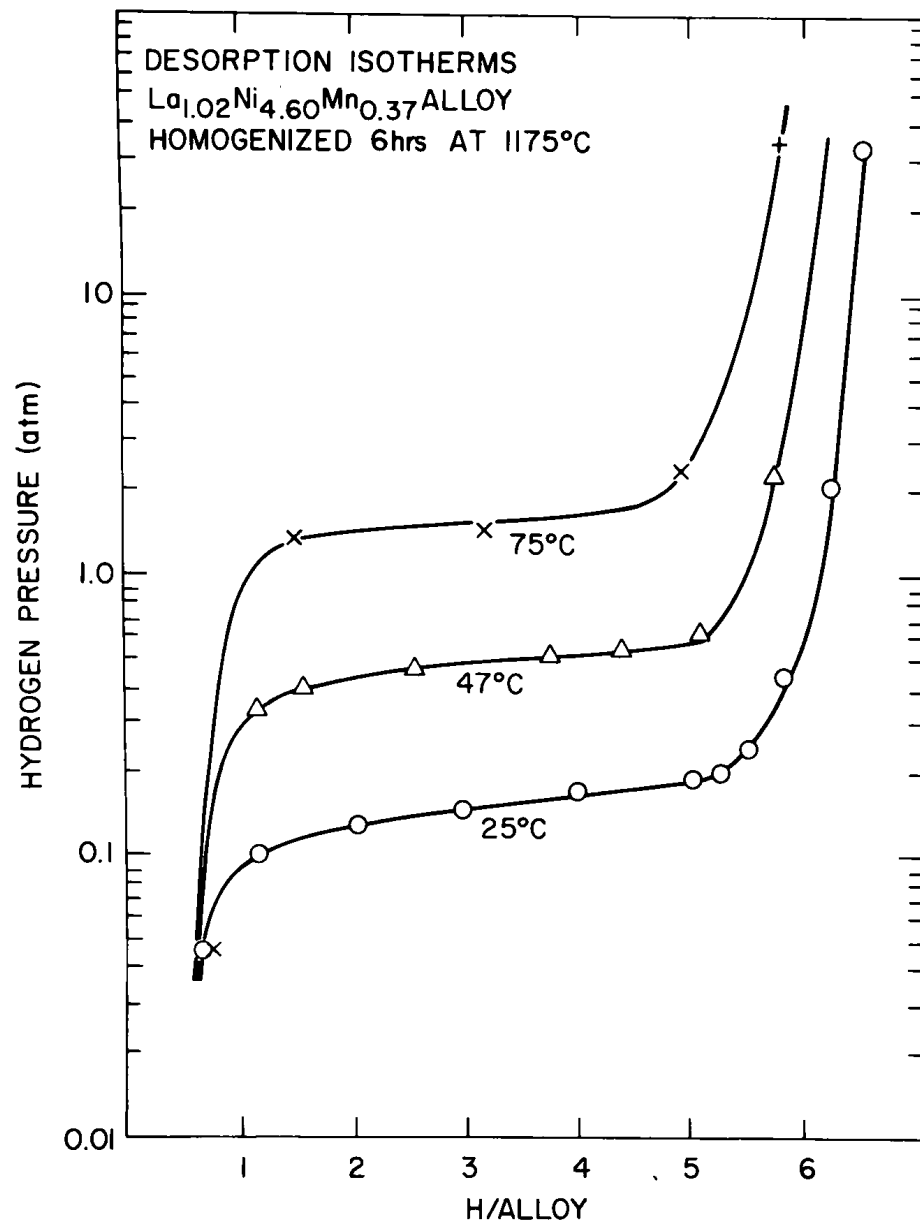


Fig. 21

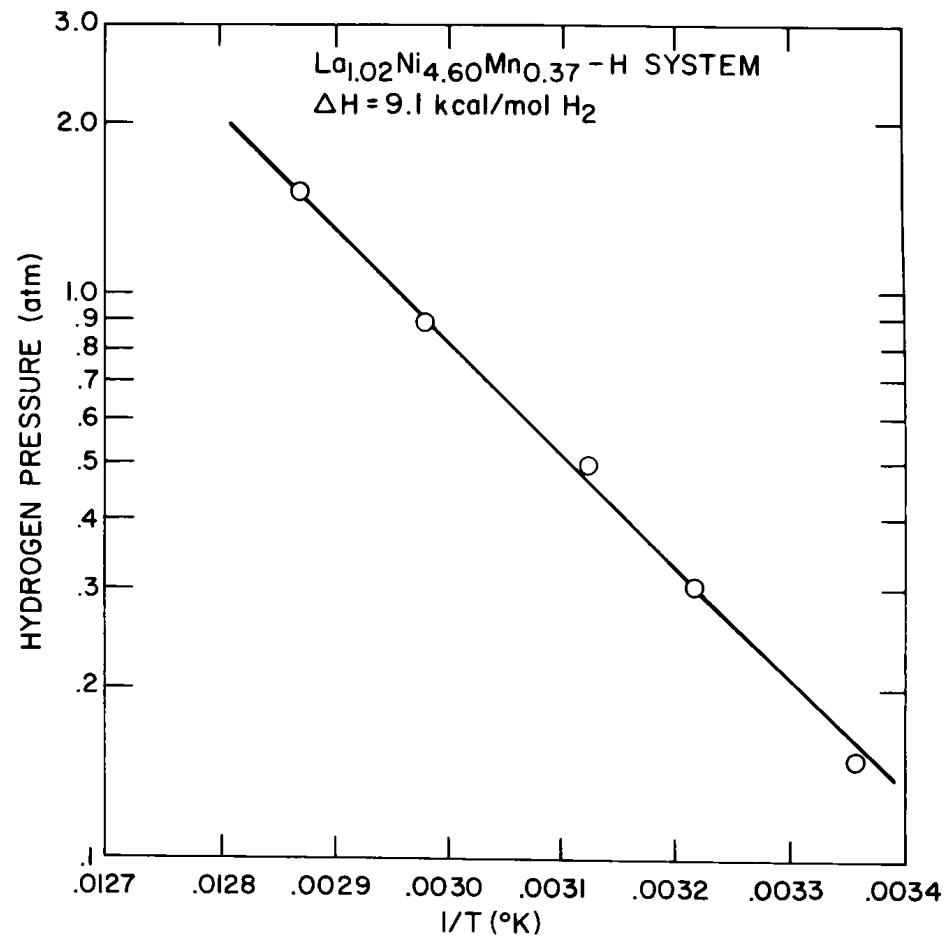


Fig. 22

The La-Ni-Mn-H System

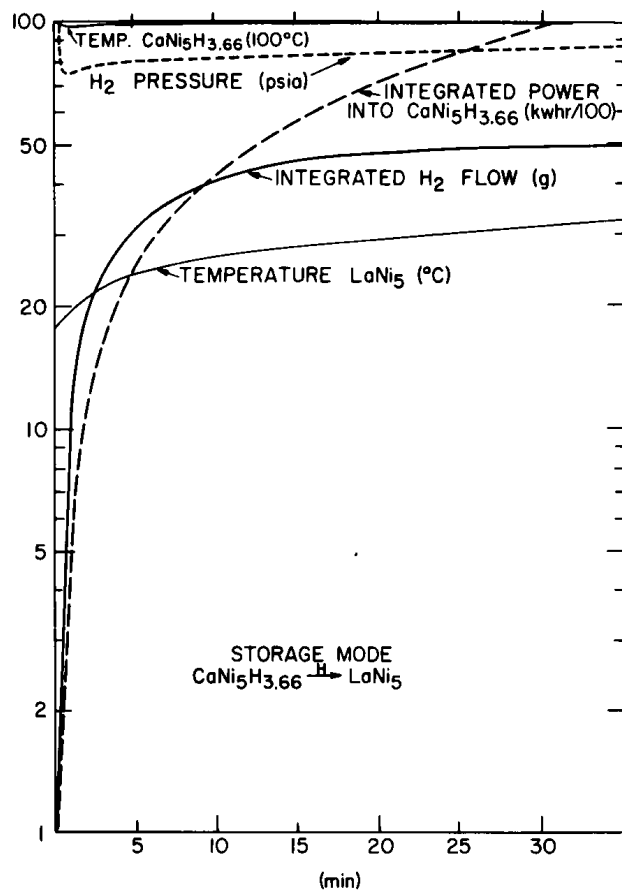


Fig. 23

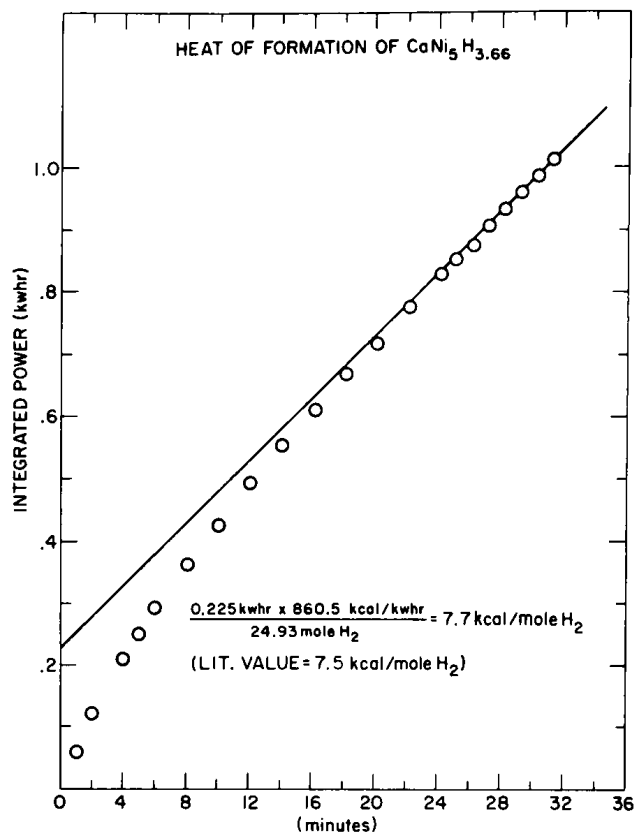


Fig. 24

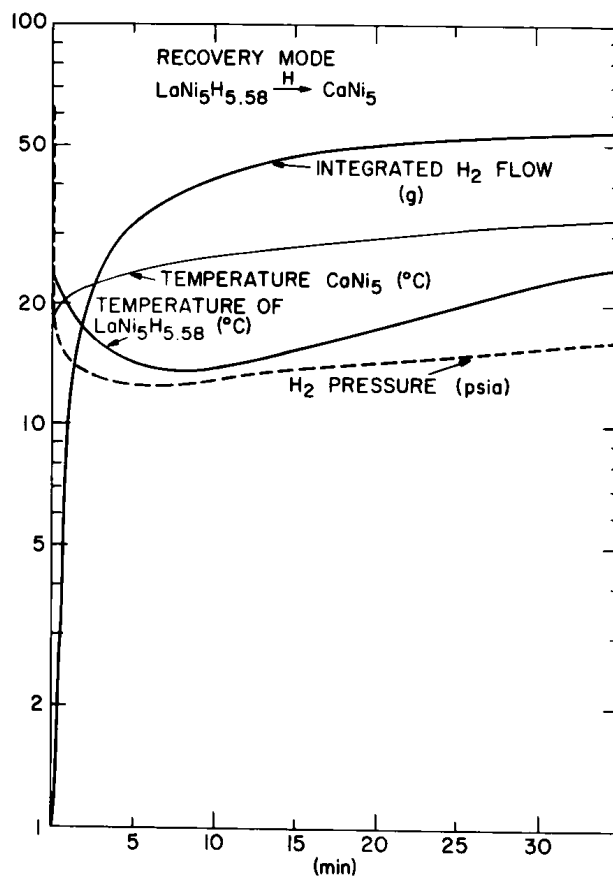


Fig. 25

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I. Sheft (82)
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